

# The Determination of As in Samples Containing High Concentrations of Chloride by ICP-MS

## Technical Note

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### Introduction

One of the main advantages of ICP-MS over ICP-AES is its relative freedom from spectral interferences. There are, however, a few cases where spectral overlap is a problem. One example is the determination of As in samples containing high (%) levels of chloride. The polyatomic ion  $^{40}\text{Ar}^{35}\text{Cl}$  interferes with  $^{75}\text{As}$ , and in addition  $^{40}\text{Ar}^{37}\text{Cl}$  interferes with  $^{77}\text{Se}$ . The interference of ArCl on Se is not a problem since a different Se isotope can be selected. As, however is monoisotopic, so no alternate isotope is available. One method to overcome such polyatomic overlaps is to resolve the interference using high resolution. In this case, however, a resolving power of  $>7500$  is required to effectively separate As and ArCl. At this resolution, ion transmission is only  $\sim 1\%$  of the transmission at unit mass resolution and so detection limits are compromised.

The 4500 ICP-MS offers the precise, routine determination of As

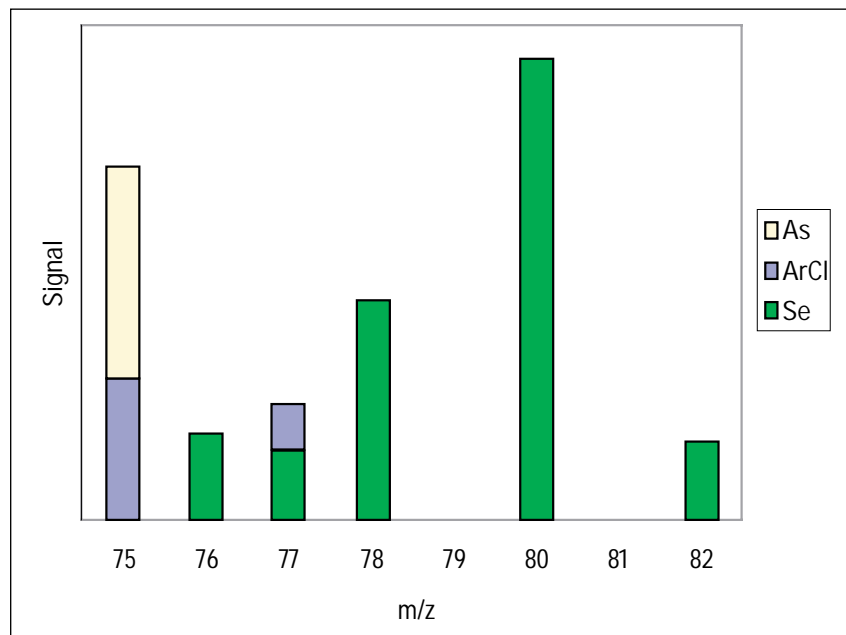


Fig. 1  
Isotopic patterns of As, Se and ArCl

even in very high concentrations of chloride by the use of mathematical correction. Elemental (interference correction) equations resident in the 4500 ICP-MS ChemStation software correct for the interferences on both As and Se simultaneously. Most importantly, the inherent ion signal sta-

bility of the 4500 ICP-MS allows for very precise correction, making it possible for the 4500 ICP-MS to determine As at the ppb and sub-ppb level even in 5% HCl. This technical note examines the effect of increasing Cl concentration on the observed As signal, and determines the ability of the 4500 ICP-



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MS to measure As in HCl. The derivation and use of elemental equations is also explained.

## Elemental equations

In samples containing chloride, the ion signal measured at mass 75 is the sum of  $^{75}\text{As}$  and  $^{40}\text{Ar}^{35}\text{Cl}$ . This is shown in Fig. 1, which depicts the elemental ratios of As, Se and ArCl. This diagram is for graphical representation only; the intensities of the bars are arbitrary and do not relate to concentration values of each individual species. Also,  $\text{Ar}_2$  species have been omitted for clarity. The ratio of the ArCl species at masses 75 and 77 is the same as the ratio of the Cl isotopes at masses 35 and 37. Therefore, the signal intensity of ArCl at mass 75 can be derived from the ArCl signal at mass 77. However, Se also has an isotope at mass 77, so the presence of Se will increase the observed signal at mass 77. Thus the contribution of Se to the total signal intensity at mass 77 must also be calculated using an alternate Se isotope. For Se correction, mass 82 is normally chosen, since the 78 and 80 isotopes suffer interference from  $\text{Ar}_2$ . In practice, this correction is simply and automatically performed by the ChemStation software using elemental equations. In this example, the equation given in EPA method 200.8 (trace metals in drinking water and wastewater by ICP-MS) was used and is shown in Fig. 2.

## Influence of Cl Concentration on As Signal

To study the effectiveness of using elemental equations to correct for Cl interference, a series of 1  $\mu\text{g/l}$  (ppb) As solutions were spiked with Cl at 0, 100, 200, 500 and

$$\begin{aligned} &\text{As signal intensity (mass 75)} \\ &= 1.000 * (^{75}\text{C}) - 3.127[(^{77}\text{C}) - (0.815) * (^{82}\text{C})] \\ &= 1.000 * (^{75}\text{C}) - 3.127 * (^{77}\text{C}) + 2.549 * (^{82}\text{C}) \end{aligned}$$

( $^{\text{M}}\text{C}$ ): ICP-MS signal (counts) at mass M

Fig. 2  
Elemental equation for As

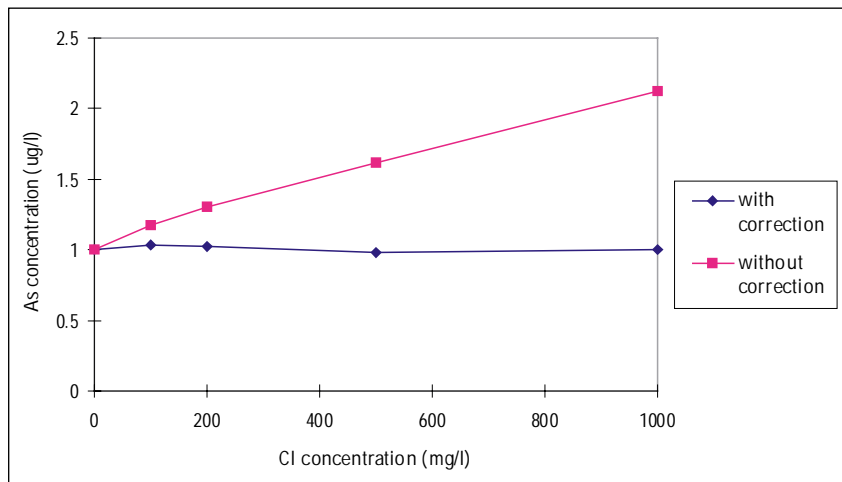


Fig. 3  
Influence of Cl on As signal

1000 mg/l (ppm). The solutions were measured for As, both with and without the use interference correction. A plot of observed As concentration vs. added Cl is shown in Fig. 3. Without correction, the observed As signal increased with added Cl, as expected. At 1000 mg/l Cl, the apparent increase in As was approx. 1  $\mu\text{g/l}$ . Using interference correction, however, no increase in As concentration was reported, demonstrating the effectiveness of interference correction. The 4500 ICP-MS generates a very stable ion signal from both elemental and polyatomic ions, allowing precise, reproducible correction for ArCl. Ion signal stability (typically <1%RSD over 2 hours) is due mainly to the mechanical and electronics design of the 4500 ICP-MS, but also partly

due to the precise temperature control of the spray chamber ( $\pm 0.1$   $^{\circ}\text{C}$ ), enabling a very stable sample aerosol to be generated.

## Determination of As in Cl Matrix

To study the effectiveness of applying interference correction to the quantitative determination of As in a chloride matrix, a series of standard solutions in a 5% HCl matrix were prepared. The As concentrations were 0, 1, 5, 10, 50, 100 and 200  $\mu\text{g/l}$ . The standards were measured using the 4500 ICP-MS - the operating parameters used are given at the bottom of this page. No internal standards were used. Calibration plots for As were constructed, both with and without interference correction selected. The data was

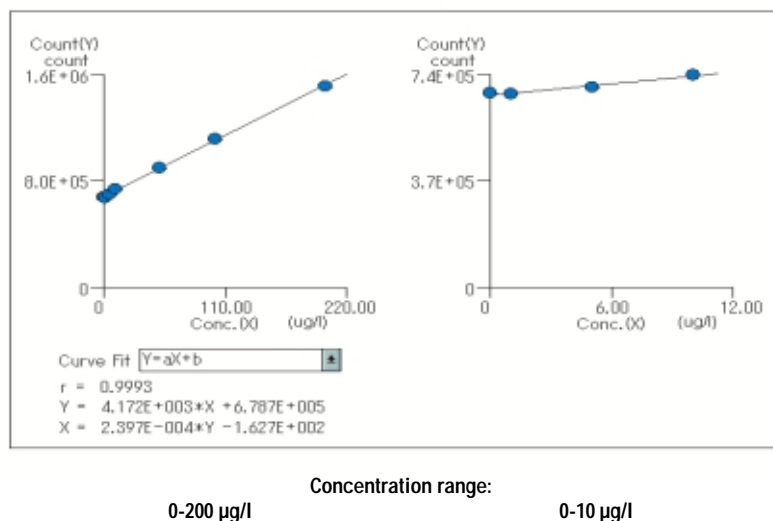


Fig. 4-1  
As calibration plots in 5% HCl without interference correction

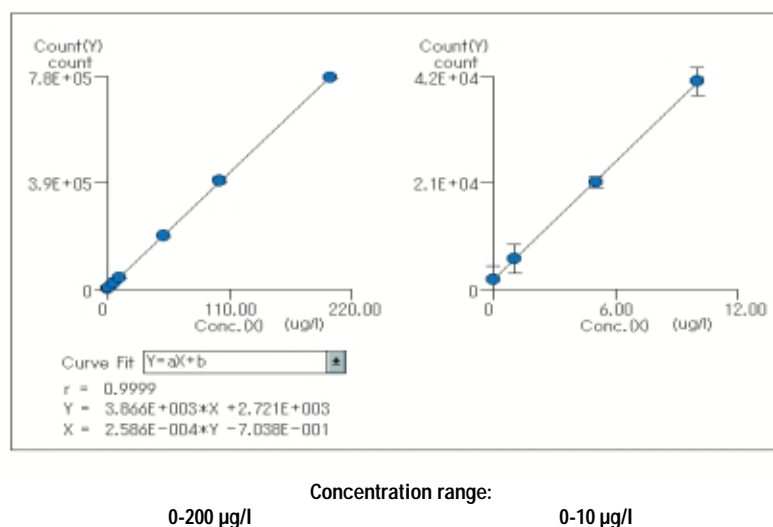


Fig. 4-1  
As calibration plots in 5% HCl with interference correction

not blank subtracted. The plots shown in Fig. 4-1 were generated without applying interference correction. Although the correlation was good, the high background due to ArCl can be seen. The scale is expanded on the right to show the low concentration points. Below 10  $\mu\text{g/l}$ , the calibration plot becomes essentially flat. In contrast, when interference correction is applied (Fig. 4-2), excellent correlation and linearity were obtained, even at the 1  $\mu\text{g/l}$  level. Clearly, the combination of interference correction and good ion signal stability (elemental and polyatomic) allow the 4500 ICP-MS to precisely determine As even in a chloride matrix. The ability to detect As at sub-ppb levels in the presence of chloride is particularly important to the study of toxic metals in foods, biomedical, environmental and clinical applications. In addition, the demonstrated ability of interference correction to compensate for polyatomic overlap at low ion concentrations can be applied to other classic ICP-MS interferences. Other interferences will be studied in future Agilent Technical Notes.

## Operating conditions

RF power	: 1.3 kW
Sampling depth	: 8 mm
Plasma gas	: 16 l/min.
Auxiliary gas	: 1.0 l/min.
Carrier gas	: 1.15 l/min.
Nebulizer	: Concentric type

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